



Influence of ultrasonic waves on the formation of lead-acid batteries

V. Naidenov*, U. Markov

Institute of Electrochemistry and Energy Systems, Bulgarian Academy of Sciences, Acad. G. Bonchev Street, Bl. 10, Sofia 1113, Bulgaria

H I G H L I G H T S

- Application of ultrasonic waves during formation.
- Ultrasonic excitation facilitates the crystallization processes.
- Application of the ultrasonic waves increases the content of PbO_2 in the positive plates.

A R T I C L E I N F O

Article history:

Received 12 March 2012

Received in revised form

17 May 2012

Accepted 5 June 2012

Available online 12 June 2012

Keywords:

Lead-acid batteries

Separators

Formation

Ultrasonic waves

A B S T R A C T

The processes of the formation of the positive and negative plates in lead batteries are slow because during the flow of the electric current through them a converting of one type of solid phase into another is done. In the formation of the plates in lead batteries there run reactions of decomposition of water from the electrolyte by separating hydrogen on the negative plates and oxygen on the positive ones. This paper presents the results of a research on the impact of the ultrasonic waves on the composition and structure of the positive and negative plates in lead-acid batteries during their formation. It is established that when applying ultrasonic waves during the formation, a high content of PbO_2 is formed at the positive plates which facilitates the separation of the absorbed gas layers of the slab and reduces the voltage of the cells. The application of ultrasonic waves during the formation creates conditions for an effective operation of the crystallization processes of the solid phases in the plates, thus shortening the time for the formation of the positive and negative plates in lead batteries and reducing the energy consumption.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

The development of the alternative energy sources expands the possibilities of the application of lead batteries as warehouses for the storage of electricity. The application of physical agents during the operation and the production of lead batteries is one of the new guidelines in the development and improvement of this type of secondary sources of electricity.

The ultrasonic waves create the possibility of external influence on the processes that occur during the charging, discharging and the formation of the positive and negative plates in lead batteries. However, there are few data in literature and present studies describing the impact of the application of ultrasonic waves during the processes of formation, charging and discharging of lead-acid battery types.

The process of the formation of positive and negative plates in lead batteries is preceded by a soaking process in which some

reactions are carried out such as sulfatization of PbO and basic lead sulfates, formed as the slab layers of PbSO_4 and PbOPbSO_4 . These reactions depend mainly on the concentration of the H_2SO_4 , from the phase of the composition of the pastes, which are described in papers [1–6]. The content of lead sulfate in the early formation is of primary importance for the subsequent development of the molding processes of the positive and negative plates in lead-acid batteries.

D. Pavlov and collaborators in their papers [4,7,8] have shown that the formation of the positive plates in which changes were made in the phase and in the chemical composition of the mature paste in them, occurs in two stages.

In papers [4,6,7,9] it has been shown that in the reactions during the first stage of the formation mainly αPbO_2 is formed because the solution in the pores of the plates is neutral, while in the second stage of the formation of the positive plates PbSO_4 is oxidized to βPbO_2 as the formed H_2SO_4 diffuses into the electrolyte. During the two stages of the formation of the positive plates, the distribution of αPbO_2 and βPbO_2 in the plates depends on the conditions for the preparation of the positive paste, the concentration and soaking time for the plates in H_2SO_4 , as well as on temperature and current for the formation.

* Corresponding author. Tel.: +359 29792796; fax: +359 28731552.
E-mail address: v_naid@abv.bg (V. Naidenov).

When applying ultrasonic waves during the formation of the positive plates of the lead batteries some conditions are created for the exchange of the electrolyte in the pores of the plates and the electrolyte in the cell volume. The improved conditions for the exchange of the electrolyte in the pores of the positive plates and electrolyte volume in the cell that have different concentrations, leads to a higher contents of βPbO_2 in these areas compared to the contents of βPbO_2 in the positive plates, which have been formed without the application of ultrasonic waves.

The formation of the negative plates also occurs in two stages, which is described in papers [4,6,10,11]; at the end of the formation certain reactions such as the decomposition of water on the negative plates into H_2 and O_2 on the positive plates take place. The absorbed gas layers are received on the surfaces of the plates which increases the cell voltage due to the increased polarization of the lead cells. This increasing of the voltage of the lead cell is represented by the equation;

$$U_{\text{cell}} = E + \eta \quad (1)$$

In the application of ultrasonic waves during the formation it is easier to separate the gas absorption layer from the surface of the plates and so polarization is reduced and hence the cell voltage U_{cell} . As a result of this the value of the electricity energy W_U put in the formation of lead plates and presented as a sum of the used energy W_E and the loss in the polarization of the electrodes W_η , is lowered.

$$W_U = W_E + W_\eta \quad (2)$$

As mentioned above in literature there are almost no publications that present the results of studies describing the impact of the application of ultrasonic waves during the processes of formation, charging and discharging of lead-acid batteries. Basically in literature there are patents that are related to external influences on electrochemical power sources. Some of them are related to the applications of the physical effects due to different sound, electromagnetic and mechanical damages used mainly to characterize ready lead batteries after their production. This is an US patent [12] according to which ultrasonic waves are used to characterize the overall assembly of the battery after its manufacture. Another US patent [13] of Active Grid Technology Inc. company also concerns the application of ultrasonic waves, but this application takes place during the exploitation attempting to remove the degradation of the active masses in the plates of the lead-acid batteries and to increase the effectiveness of the charging and discharging in the process of their cycling.

Specifically, the use of ultrasonic waves in the formation of the plates in the lead-acid batteries is offered in the Japanese Patent of Shin Kobe Machinery [14]. According to this patent, the authors propose the application of ultrasonic waves during the formation for about 5 min at a certain time in order to remove the absorbed gases on the surfaces of the plates.

This paper aims to show that the application of ultrasonic waves during the formation process of the lead batteries, creates conditions for the flow of electrochemical and crystallization processes that form the composition and structure of the lead and lead-dioxide plates of different composition and structure of the plates which are formed without the influence of ultrasonic waves. Moreover, the paper shows that this method of formation reduces the polarization in the lead cells.

2. Experimental

2.1. Test cells

For the purposes of this study we assembled 10 test cells comprising one positive and two negative unformed plates. The

selected unformed positive and negative plates were of equal weight and were taken from a batch of the regular production of the Bulgarian battery plant MONBAT; the dimensions of the positive plates were: width 148 mm, height 116 mm and thickness 2 mm, the dimensions of the negative plates: width 148 mm, height 116 mm and thickness 1.8 mm. The capacity of the positive plates of the test cells was 9.5 Ah at 50% utilization of the positive active mass. The test cells were of the flooded type with standard polyethylene pocket separators. H_2SO_4 solution with 1.25 g cm^{-3} density was used as electrolyte for the formation process; the same amount of electrolyte was poured in all test cells. The formation of half of the test cells was performed with no ultrasonic excitation and the other 5 cells were formed by applying ultrasonic waves.

2.2. Formation program

At the beginning of the formation process, all test cells were flooded with H_2SO_4 electrolyte and were left to soak for 2 h. After that, 5 cells were put into an ultrasonic bath type RK 512 H produced by the German company "Bandelin" with the capacity of 16 L and power consumption of 450 W with 860 W ultrasonic peak power and 35 kHz frequency.

The flooded test cells were subjected to formation employing a formation program comprising four initial steps, each with a duration of 20 min and currents $I_1 = 0.478 \text{ A}$; $I_2 = 0.77 \text{ A}$; $I_3 = 1.1 \text{ A}$ and $I_4 = 2 \text{ A}$, respectively. Then, a formation with a current $I_5 = 4.31 \text{ A}$ until the cell voltage reached $U_{\text{Form1}} = 2.75 \text{ V}$. Further formation was conducted potentiostatically at a constant voltage of $U_{\text{Form1}} = 2.75 \text{ V}$. The formation of the test cells continued under these conditions until a capacity equal to 1.5 times the theoretical capacity, which corresponds to $Q_{\text{Form1.5}} = 28.5 \text{ Ah}$ was reached. Five of the test cells were formed under a constant application of ultrasonic waves and the other 5 cells were formed without ultrasonic excitation. On completion of the formation process, without correction of the H_2SO_4 electrolyte density, the test cells were set to cycling tests employing the following cycling profile:

- charge with current $I_{\text{ch1}} = 3 \text{ A}$ up to cell voltage $U_{\text{ch1}} = 2.62 \text{ V}$ with charge factor 110% followed by further charging at $U_{\text{ch2}} = 2.50 \text{ V}$ until 115% charge factor was reached.
- discharge with current $I_{\text{disch1}} = 0.95 \text{ A}$, corresponding to 10 h discharge rate, until the end-of-discharge voltage was $U_{\text{EOD}} = 1.70 \text{ V}$.

Bitrode (USA) testing equipment was used for the cycling tests of the experimental lead cells.

The temperature of the cells during the formation process, with and without ultrasonic excitation, was kept within the range $35\text{--}40^\circ\text{C}$ through the temperature of the water in the ultrasonic bath. The cycling tests of all cells were conducted in thermostatic water baths at constant temperature of 25°C .

3. Results and discussion

3.1. Defining the effect of the application of ultrasonic waves on the current, voltage and duration of the lead cell formation process

The current curve during the formation of the 9.5 Ah test cells, as well as the changes in cell voltage and time of formation with and without ultrasonic application, are presented on Fig. 1.

It can be seen from the figure that at set constant current $I_5 = 4.31 \text{ A}$, the voltage limit of $U_{\text{Form1}} = 2.75 \text{ V}$ is reached 14.25 Ah passed charge for the cells formed without ultrasonic excitation (Fig. 1a). Further the formation continues at a constant voltage $U_{\text{Form1}} = 2.75 \text{ V}$ and, as evident from the figure, the current of these

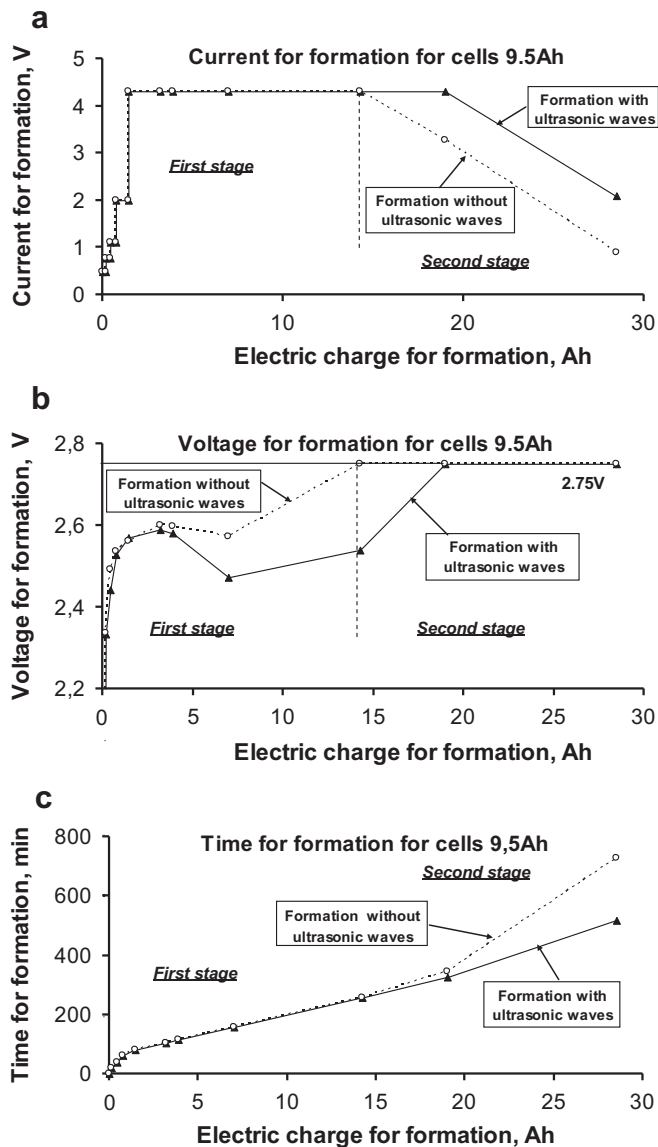


Fig. 1. Changes in formation current, cell voltage and time of formation versus electric charge for formation of 9.5 Ah lead-acid cells with and without application of ultrasonic waves.

cells begins to decrease. At the same time, the cells formed with the application of ultrasonic waves reach the preset voltage limit $U_{\text{Form1}} = 2.75$ V after 19 Ah passed charge with the same current $I_5 = 4.31$ A. After that, the formation of these cells continues at a constant voltage $U_{\text{Form1}} = 2.75$ V and, as can be seen from the figure, their current begins to decrease. The measured difference in the formation current between the cells formed with applying ultrasonic waves and those formed with no ultrasonic excitation is about 1 A at applied charge of 19 Ah and about 1.2 A at the end of the formation process, when 28.5 passed charge at a constant voltage of $U_{\text{Form1}} = 2.75$ V.

At the end of the second stage of the formation of the test cells, oxygen is evolved on the positive plates which may form an absorption gas layer on the surface on the positive plates, while on the negative plate, an evolution of hydrogen starts which may also form a gas layer on the surface of the negative plate. The results presented in (Fig. 1a) suggest that the application of ultrasonic waves after an applied charge of 14.25 Ah during the formation

process of lead-acid cells probably facilitates the desorption of the gas layer from the surface of the positive electrode leading to a decrease of the internal resistance of the cell and thus increasing the rate of the electrochemical reactions.

Fig. 1b illustrates the changes in the cell voltage during the formation of the test cells. During the first stage of the formation up to the application of a charge of 3.2–3.9 Ah, the voltage of the two types of cells do not differ. It can be seen from the figure that after 7 Ah passed charge, the cells formed with application of ultrasonic waves have a voltage lower by about 100 mV than that of the cells formed without ultrasonic excitation, and this difference increases to about 200 mV at the same applied charge of 14.25 Ah. The data in Fig. 1b also indicate that the cells formed with the application of ultrasonic waves reach the preset formation voltage limit of $U_{\text{Form2}} = 2.75$ V after an applied charge of 19 Ah, while the cells formed without the application of ultrasonic waves reach this voltage limit after an applied charge of 14.25 Ah. This experimental finding could be explained by the data presented in Fig. 1a, according to which the applied ultrasonic waves facilitate the desorption of the gas layer from the surface of the positive

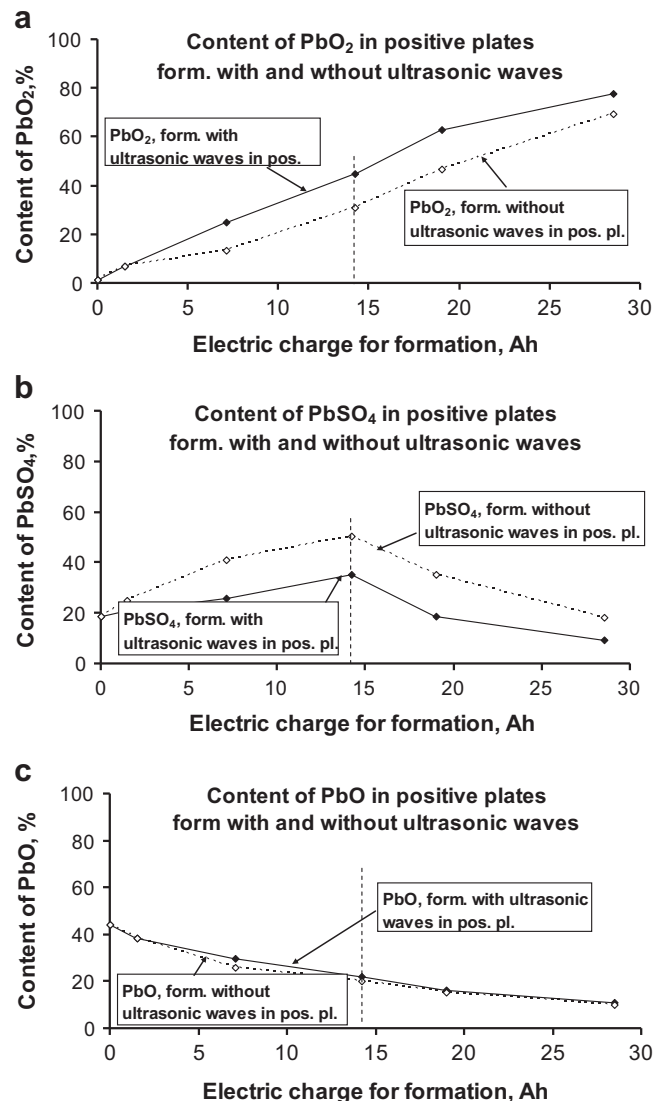


Fig. 2. Changes in chemical composition of the positive plates of the test cells during different stages of the formation process with and without application of ultrasonic waves.

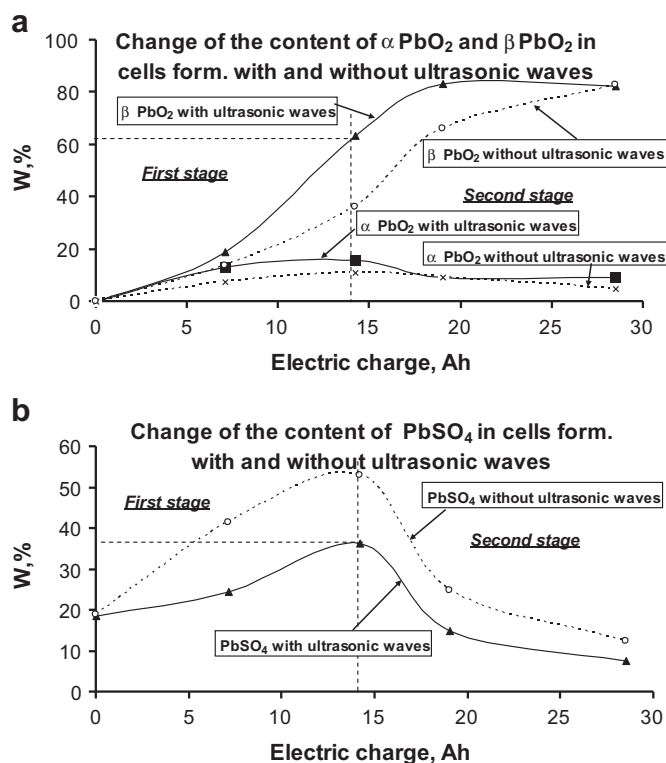


Fig. 3. Changes of the content of α PbO₂, β PbO₂ and PbSO₄ phases in the positive plates of the test cells, measured through XRD analysis, during formation with and without ultrasonic excitation.

electrode at the end of the second formation stage. Hence, the cells formed with application of ultrasonic waves have lower voltage at the end of the formation process as compared to those formed with no ultrasonic excitation.

The experimental results presented in Fig. 1b give grounds for the hypothesis that the application of ultrasonic waves at the beginning of the formation process facilitates the exchange of ions and water between the positive and negative plates and the bulk of the electrolyte, thus facilitating the processes of the formation of PbO₂ and Pb, which proceed under lower voltages at the same formation currents $I_5 = 4.31$ A.

Fig. 1c shows the formation time needed to reach 1.5 times the theoretical capacity of the test cells, namely 28.5 Ah. The data in the figure indicate that the formation time is almost the same for all cells up to the applied charge of 19 Ah, but after that the cells formed without the application of ultrasonic waves need more time to reach the preset capacity 28.5 Ah because the formation current is lower. The figure shows also that the cells formed with application of ultrasonic waves reach capacity of 28.5 Ah after 8 h and 35 min of formation, whereas those formed without ultrasonic excitation need 12 h and 8 min of formation to reach the same capacity of 28.5 Ah.

3.2. Defining the PbO₂, Pb, PbSO₄ and PbO content in the positive and negative plates at different formation stages and at the end of the formation process of the test cells

The content of PbO₂, PbSO₄ and PbO in the positive and negative plates is determined by a chemical analysis and the obtained results are presented in Fig. 2.

Fig. 2a shows the changes in PbO₂ content in the positive plate during the formation: at an applied charge of 1.5 Ah, 7.1 Ah, 14.25 Ah, 19 Ah, and at the end of the formation process, i.e. when a charge of 28.5 Ah was applied to the cell. It can be seen that even at the beginning of the formation process, after an applied charge of 7.1 Ah, the content of PbO₂ in the positive plates of the cells formed with the application of ultrasonic waves is higher by 12% than that of the cells formed with no ultrasonic excitation. This tendency is sustained further on in the formation, the difference being 14% at the applied charge of 14.25 Ah, 16% at an applied charge of 19 Ah

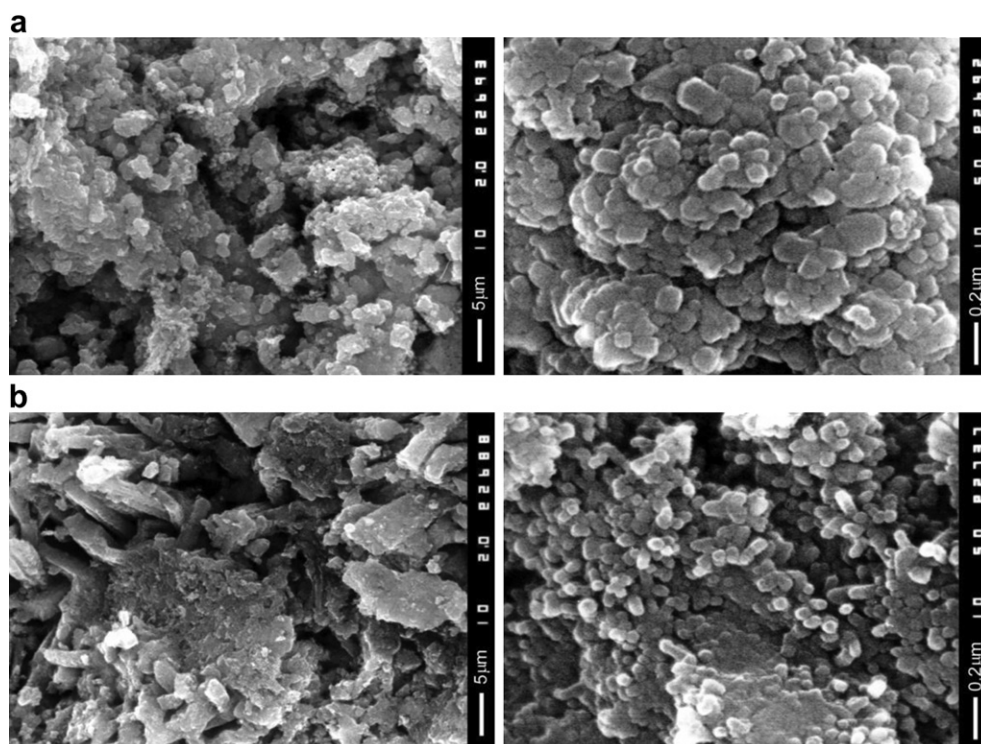


Fig. 4. SEM micrographs of the positive active mass formed: (a) without application of ultrasonic waves and (b) with ultrasonic excitation.

and 8% at the end of the formation process, i.e. at an applied charge of 28.5 Ah, respectively.

The results of the chemical analysis of the PbSO_4 content in the positive plates of the test cells at different stages of formation and at the end of the formation process are presented in Fig. 2b. It should be pointed out that in our investigation the cells were set to preliminary soaking in sulfuric acid solution of 1.25 g cm^{-3} density for 2 h. During this pre-treatment, sulfation of PbO to PbSO_4 proceeds up to about 20% PbSO_4 content, including also the PbSO_4 in the 3BS phase of the cured paste. These results are in agreement with the experimental data reported in reference [4]. Fig. 3b shows the changes in the percentage content of PbSO_4 in the positive plates of the test cells during the different stages of formation, with and without an application of ultrasonic waves. The data in the figure indicate that the plates formed with ultrasonic excitation have lower PbSO_4 content than their counterparts formed without an application of ultrasonic waves throughout the formation process, the difference being about 15% at an applied charge of 7.1 Ah, 15% at applied charge of 14.25 Ah, 16% at applied charge of 19 Ah and 9% at the end of the formation process, i.e. at 28.5 Ah passed charge, respectively.

The changes in PbO content in the positive plates (determined by the chemical analysis), at different stages and at the end of the formation process, are presented in Fig. 2c. There is almost no difference in the content of PbO in the positive plates when formed with and without ultrasonic excitation. This means that the application of ultrasonic waves during the formation of the positive active mass of lead-acid cells does not influence the transformation reaction of the formation PbO_2 from PbO , which depends entirely on the concentration of the sulfuric acid solution in the pore volume and on the formation of the current density.

Very indicative about the effect of ultrasonic waves is the change in αPbO_2 and βPbO_2 content in the positive plates during the formation of the test cells. Fig. 3a presents the results from the XRD analysis determining the content of αPbO_2 and βPbO_2 phases in the positive active mass at different stages of formation. When ultrasonic waves are applied, the quantity of βPbO_2 in the active mass increases after an applied charge of 7.1 Ah, i.e. 0.37% of the theoretical capacity. The data in Fig. 3a indicate that between an applied charge of 14.25 Ah and an applied charge of 19 Ah, βPbO_2 content in the plates formed with ultrasonic waves excitation is higher by 25% than that in the positive active mass of the cells formed without the application of ultrasonic waves. It is a well known fact that during the first formation stage the electrolyte in the pores of the positive plates becomes neutral and αPbO_2 is formed. In our experiment, however, the application of ultrasonic waves during the first formation stage facilitates the exchange of H^+ , SO_4^{2-} and H_2O flows in the volume of the active mass and the release of electrons from the Pb^{2+} ions, which results in the formation of greater amounts of βPbO_2 in the positive plates of the cells formed with an application of ultrasonic waves. This effect gradually decreases after 19 Ah passed charge and, at the end of the formation process, the content of βPbO_2 in the positive plates formed with and without an application of ultrasonic waves becomes equal.

Fig. 3b also shows that, apart from the increase of the βPbO_2 content in the positive plates during the formation with ultrasonic waves excitation, a decrease of the quantity of PbSO_4 in the positive plates (as determined from the relative intensities of the XRD peaks) is observed as compared to the plates formed without an application of ultrasonic waves. As evident from the figure, this difference is about 30% between 7.1 Ah and 14.25 Ah passed charges, i.e. the same as the difference between the quantities of αPbO_2 and βPbO_2 in the positive plates. Then the difference decreases to 15% at an applied charge of 19 Ah and reaches down to 4% at the end of the formation process, i.e. at 28.5 Ah passed charge.

The above experimental data indicate that the application of ultrasonic waves during the formation of lead-acid cells facilitates the electrochemical reactions of the formation of PbO_2 from PbSO_4 .

Fig. 4 shows SEM micrographs of positive active mass formed without ultrasonic waves excitation (Fig. 4a) and with application of ultrasonic waves (Fig. 4b). The SEM images in Fig. 4a feature PbO_2 particles coalesced into agglomerates and aggregates, whereas the PAM formed with ultrasonic waves excitation (Fig. 4b) comprises separate small PbO_2 crystals yielding a higher active mass surface, which is confirmed also by the results of the BET surface measurements presented in Fig. 7.

The content of Pb , PbSO_4 and PbO in the negative plates of the test cells at different stages and at the end of the formation process, as determined by chemical analysis, is presented in Fig. 5.

Fig. 5a shows the changes in Pb content in the negative plates after applied charge respectively of 1.5 Ah, 7.1 Ah, 14.25 Ah and 19 Ah, and at the end of the formation process, i.e. at 28.5 Ah passed charge. The data in this figure indicate that the application of ultrasonic waves during the formation of the negative plates does

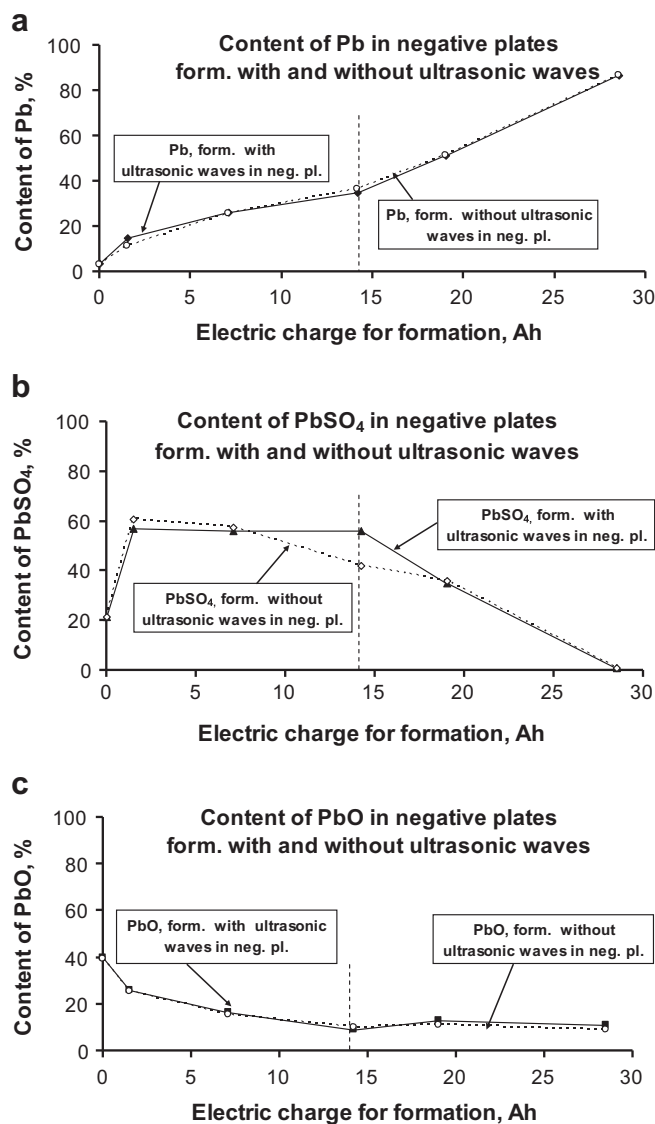


Fig. 5. Changes of the content of Pb , PbSO_4 and PbO in the negative plates of the test cells during different stages of the formation process with and without application of ultrasonic waves.

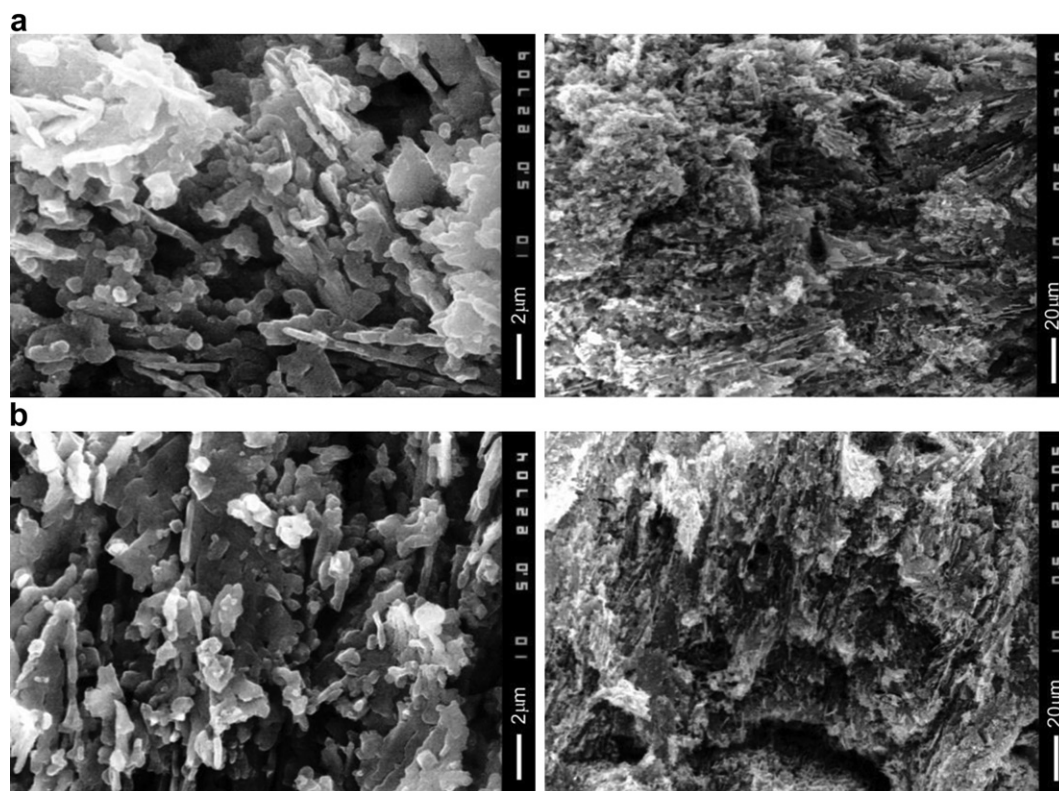


Fig. 6. SEM micrographs of the negative active mass formed: (a) without application of ultrasonic waves and (b) with ultrasonic excitation.

not influence the electrochemical and crystallization reactions of Pb formation. At the beginning of the formation, there is no difference in the content of Pb in the negative plates formed with or without application of ultrasonic waves.

Fig. 5b presents the obtained results from the chemical analysis for the content of PbSO_4 . A difference in the percentage content of PbSO_4 in the negative plates is observed only at applied charge of 14.25 Ah, namely the sulfate content in NAM is lower by 6% when the cells are formed with an application of ultrasonic waves. At all other stages of the formation process, irrespective of whether or not ultrasonic excitation is applied, the PbSO_4 content in the negative plates of the flooded test cells is the same.

And finally, Fig. 5c presents the experimental data about the content of PbO in the negative plates of the test cells at different stages and at the end of the formation process with and without an application of ultrasonic waves. The curves for the two types of cells coincide, which indicates that the ultrasonic wave does not affect the reactions involving PbO of the formation process and hence its content in NAM does not change under the influence of ultrasonic waves.

Based on the experimental results presented in Fig. 5a, b and c, it can be concluded that application of ultrasonic waves during the formation of flooded lead-acid cells does not facilitate the progress and efficiency of the reactions of the negative active mass formation.

Fig. 6a shows SEM micrographs of negative plates formed without ultrasonic excitation (Fig. 6a) and with the application of ultrasonic waves (Fig. 6b). As evident from the SEM images, there are no substantial differences in the size and distribution of Pb crystals in the volume of the two types of active masses.

It can be generally concluded that the application of ultrasonic waves during the formation of lead-acid cells influences the electrochemical reactions of formation and the crystallization

processes in the positive plates, and hence the content and structure of the positive active mass, but has an insignificant effect on the formation processes and thus on the structure of the negative active mass. This conjecture is also confirmed by the results from the BET measurement of the specific surface of the positive and negative active masses of cells formed with and without an application of ultrasonic waves. These results are presented in Fig. 7.

The curves in Fig. 7 show that when ultrasonic waves are applied during the formation of lead-acid cells, the positive active mass has a higher specific surface area by about $2 \text{ m}^2 \text{ g}^{-1}$ than that of the PAM formed without ultrasonic waves excitation throughout the formation process. The data in the figure indicate also that the

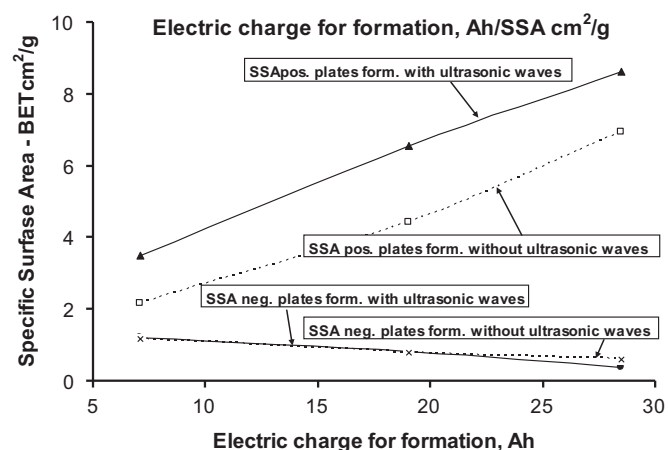


Fig. 7. BET specific surface area of the positive and negative active masses of lead-acid cells formed with and without application of ultrasonic waves.

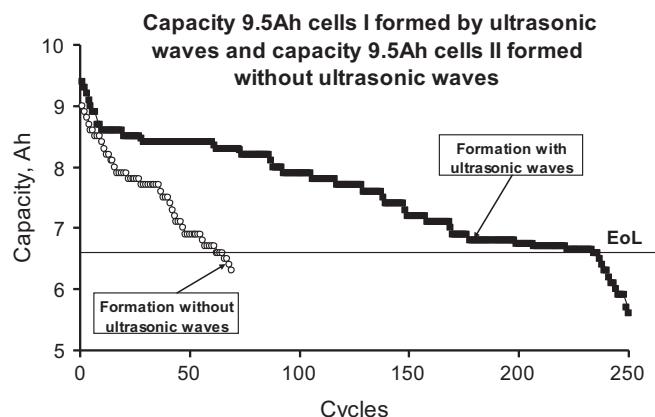


Fig. 8. Averaged values from the capacity measurements of the 10 flooded test cells with 9.5 Ah capacity, formed with and without application of ultrasonic waves.

specific surface area of the negative active mass remains almost unchanged during the formation of the test cells, irrespective of whether or not ultrasonic waves are applied. These results come to confirm once again the conclusion that the application of ultrasonic waves during the formation process has an impact only on the structure of the positive active masses in lead-acid cells.

3.3. The effect of ultrasonic waves excitation during the formation of lead-acid cells on the capacity and cycle life of flooded cells

Fig. 8 presents the average results from the capacity measurements of the ten 9.5 Ah test cells on cycling. Five of the cells were formed with an application of ultrasonic waves and 5 were formed without ultrasonic excitation.

It can be seen from the data in Fig. 8 that the capacity of the cells formed without application of ultrasonic waves declines below 80% of their rated capacity, i.e. below 7.5 Ah, after about 40 cycles, while the cells formed with the application of ultrasonic waves complete about 120 cycles before their capacity reaches the end-of-life criterion of 7.5 Ah. The data in the figure indicate that the

application of ultrasonic waves during the formation of flooded cells results in a higher capacity and about three times longer cycle life of the cells on cycling.

4. Conclusions

The application of ultrasonic waves during the formation of flooded lead-acid cells changes the formation processes and the structure of the positive active mass. We suppose that ultrasonic excitation facilitates the crystallization processes in the positive plates and contributes to the release of the absorbed gas layer at the surface of the positive plates at the end of the formation, which leads eventually to an increase of the electrochemical reactions rate. Under the influence of the applied ultrasonic waves the content of PbO_2 in the positive plates increases, i.e. the efficiency of the formation process is improved and the obtained structure of the formed positive active mass ensures a higher capacity and a longer cycle life of the formed batteries.

The application of ultrasonic waves during the formation process does neither influence the electrochemical reactions rates nor the structure of the formed negative active mass.

References

- [1] V.H. Dodson, J. Electrochem. Soc. 108 (1961) 401.
- [2] J. Burbank, J. Electrochem. Soc. 113 (1966) 10.
- [3] D. Pavlov, S. Ruevski, T. Rogachev, J. Power Sources 46 (1993) 337.
- [4] D. Pavlov, Lead-Acid Batteries Science and Technology, Elsevier, Amsterdam, 2011.
- [5] D.A.J. Rand, R.M. Dell, Batteries for Electric Vehicles Research Studies, Press, Taunton, UK, 1998.
- [6] D.A.J. Rand, P.T. Moseley, J. Garche, C.D. Parker (Eds.), Valve-Regulated Lead-Acid Batteries, Elsevier, Amsterdam, 2004.
- [7] D. Pavlov, G. Papazov, V. Iliev, J. Electrochem. Soc. 119 (1972) 8.
- [8] D. Pavlov, in: B.D. McNicol, D.A.J. Rand (Eds.), Power Sources for Electric Vehicles, Elsevier, Amsterdam, 1984, p. 328 (Chapter 5).
- [9] G. Papazov, J. Power Sources 18 (1986) 337.
- [10] D. Pavlov, V. Iliev, J. Power Sources 7 (1981/82) 153.
- [11] D. Pavlov, V. Iliev, G. Papazov, E. Bashtavelova, J. Electrochem. Soc. 121 (1974) 854.
- [12] US Patent 6,520,018.
- [13] US Patent 7,592,094.
- [14] Japan Patent 11-312533.